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FRACTIONATION OF FLUORINE, CHLORINE AND OTHER TRACE ELEMENTS DURING DIFFERENTIATION OF A THOLEIITIC MAGMA

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The elements F, Cl, Ni, Co, Cu, Ga, Sc, Cr, V, Ba and Sr have been determined in two drill cores through a differentiated tholeittic dolerite sill from Tasmania. A multivariate statistical technique is employed to demonstrate the occupancy of hydroxyl lattice sites by both chlorine and fluorine. Consideration of trace-element/major element ratios suggests that, in these dolerites, Ni occupies Fe⁺² sites, Co and Sc replace both Mg and Fe⁺², Cr replaces Fe⁺³, V⁺⁴ replaces Ti, Ga replaces Al, and Ba and Sr both replace Ca.

INTRODUCTION

Tholeitic dolerites of Jurassic age are of widespread occurrence in Tasmania. Edwards (1942) has shown that these dolerites are commonly differentiated and are similar in composition to those of the Karoo, Palisades and Antarctica provinces. The effect of the limited differentiation of the Mt. Wellington sheet on the distribution of major and trace elements has been studied by Edwards (1942) and Tiller (1959); in the Red Hill intrusion, differentiation has produced silicic granophyre and this body has been studied in detail by McDougall (1962) and the variation of Ni, Co, Cr and Cu reported by McDougall and Lovering (1963).

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The structure of the Great Lake sheet has been discussed by Carey (1958) and McDougall (1964). Numerous bore holes have been drilled through this sheet and the physical and petrological properties of some of these cores studied by Jaeger and Joplin (1955), Joplin and Jaeger (1957), Jaeger and Green (1958), and McDougall (1958). McDougall (1964) has recently completed a detailed study of the petrology and major element composition of two cores from this sheet and shown that one, D.D.H. 5084, is very similar to the Mt. Wellington sheet, and the other, D.D.H. 5123, is markedly more differentiated in that granophyre has been produced in the upper 70-100 feet. These two cores, then, exhibit the complete range of fractionation found in the Tasmanian dolerites.

Although several studies of trace element variation during magmatic differentiation have been reported previously (e.g. Wager and Mitchell, 1951; Nockolds and Allen, 1956; McDougall and Lovering, 1963) the behaviour of fluorine and chlorine has not previously been examined. In view of the advantages associated with the study of bore hole material and the extensive physical, chemical and mineralogical data already available from the Great Lake dolerite sheet, an investigation of the trace element distribution in the same samples studied by McDougall should prove of fundamental importance to our understanding of the differentiation of tholeiitic magmas.

Description of the Great Lake Dolerite Sheet

The Great Lake dolerite is a large transgressive sheet of Jurassic age. Adjacent to Great Lake it is of the order of 2000 feet thick and granophyre, of very limited lateral extent, has been produced only in this area. The 5123 bore hole commenced in granophyre and grades downward into acid dolerite at a depth of 70-100 feet. Eastwards, the sheet rises steeply

and in the region of the Tiers Arch (Carey, 1958) becomes only 100-200 feet thick; further eastwards it again achieves a thickness in excess of 1200 feet. The 5084 core is from this region of the sheet. The paper by McDougall (1964) provides block diagrams illustrating the structure of the sheet and the location of the bore holes.

Modal analyses of 5123 and 5084 have been reported by McDougall (1958; 1964). The lower zone dolerites consist of approximately 45% clinopyroxene, 40% plagioclase, up to 8% orthopyroxene, 2% iron ore, with the residue being made up by a poorly crystallized mesostassis. In the central zone dolerites, orthopyroxene disappears and the proportion of clino-pyroxene steadily decreases; plagioclase and iron ore increase slightly and mesostasis increases markedly. Granophyre, found only in 5123, is formed by a rapid increase in mesostasis at the expense of the other constituents.

The pyroxene of the lower and central zone dolerites consists of equal proportions of augite and pigeonite; the plagioclase of both regions is labradorite commonly zoned to a rim of andesine. An intergrowth of quartz and alkali feldspar is rarely visible in the mesostasis of the lower zone but is somewhat more common in the central zone dolerites. Microlites of pyroxene and needles of apatite are also observed in the mesostatis of the central zone. In the granophyre, the plagioclase remains labradorite but pigeonite is absent and the pyroxene is ferroaugite.

ANALYTICAL METHODS

The analytical procedures for chlorine and fluorine have been described in detail elsewhere (Greenland and Lovering, 1964a). In brief, chlorine was determined by fusion of the powdered rock sample in an Edwards-

Urey type distillation device (Edwards and Urey, 1955) and analysis of the distillate by a micro-diffusion technique as described by Conway (1957); fluorine was determined by an emission spectrographic technique employing the CaF emission bands and the CaO bands as internal standard. In both cases, precision is approximately \$\frac{1}{2}10\%\$ of the amount present as estimated from numerous replicate analyses of a single sample.

The emission spectrographic procedure employed in the determination of Ni, Co, Cu, Ga, Sc, Cr, V, Sr, and Ba has also been described previously (Greenland and Lovering, 1964b). Samples were mixed 1:1 with graphite containing palladium as internal standard and arced in duplicate in an oxygen stream. Dilutions of the U.S.G.S. standard diabase W-1 were used as standards. The analytical precision was estimated from 14 single arcings of a dolerite scattered throughout the samples studied here; these results are shown in Table 1 expressed as a relative error.

RESULTS

The analytical results of the 5123 drill core are presented in Table 2 and of the 5084 core in Table 3. Ratios of the trace elements to certain major elements have been computed from the data of McDougall (1964) and are shown in Table 4.

It is convenient to have an index of differentiation in order to combine the data from the two bore holes. McDougall (1964) has shown that differentiation in the Great Lake sheet was controlled by fractionation in the pyroxene series and thus the mafic index, $\frac{(Fe^{+2}+Fe^{+3}) \times 100}{Fe^{+2}+Fe^{+3}+Mg}$, of Wager and Deer (1939) and Simpson (1954) provides a satisfactory measure of the degree of fractionation. This ratio has been computed by McDougall (1964) for these samples and has been included in Tables 2, 3, and 4. The combined data of these two cores have then been plotted against this index in Figures

1, 2, and 3 thus illustrating the fractionation patterns of the trace elements with differentiation; since the analytical error of the determinations is log-normally distributed, a logarithmic concentration scale has been employed.

The ionic radii and electronegativities of a number of elements have been assembled in Table 5 since these properties are generally believed to govern their fractionation during crystallization differentiation and are frequently referred to in the text.

Fluorine:

Correns (1956) has reviewed the geochemistry of fluorine and concluded that there appears to be no correlation between fluorine content and chemical composition of a rock. No study of the variation of fluorine during differentiation of a basic magma has been published and, while Correns' conclusion may be generally true, fluorine would be expected to become enriched in the most acid fraction of a differentiated sequence. According to Correns (1956), fluorine may occur as independent minerals (apatite, fluorite) or may replace hydroxyl ions in micas and amphiboles. Of these minerals, only apatite has been detected in thin sections from these cores (McDougall, 1964) and thus fluorine is presumably concentrated in the minimum sessions.

In 5123, fluorine is reasonably constant in the lower zone dolerites and increases steadily through the central zone to a maximum in the granophyres. The lower zone dolerites of 5084 are also depleted in fluorine relative to the central zone and it is apparent that crystal fractionation of the Great Lake sheet has led to enrichment of the residual magma in fluorine. Figure 1 shows that fluorine is enriched to about the same degree as barium and gallium in the final crystallates of the magma. In fact, the profile of fluorine with depth is very similar to that of barium in both cores demonstrating that

similar distributions do not necessarily imply identical lattice sites.

Although apatite is universally present in the mesostassis of these rocks, there is insufficient phosphorus to account for even half the fluorine as a pure fluor-apatite. Evidence that fluorine is replacing hydroxyl ions is presented in a later section.

Chlorine:

The distribution of chlorine through a differentiated sequence has not been described previously, but Correns (1956) has concluded that there is no general enrichment of chlorine in acid rocks relative to basic rocks. In silicate rocks, chlorine occurs predominantly in micas and hornblendes, replacing the hydroxyl ion, but may also be present as solutions in mineral inclusions or dissolved in rock glass (Correns, 1956), and thus is expected to be concentrated in the mesostassis of the Great Lake sheet.

The fractionation of chlorine in 5123 is considerably less marked than that of fluorine though the slight enrichment of chlorine in the central zone dolerites and granophyres does parallel the enrichment of fluorine. Although slightly enriched in the earliest central zone dolerites of 5084, the degree of fractionation is much less than that of fluorine or even of chlorine itself in 5123. The variation of chlorine with differentiation is shown in Figure 1 which confirms the very slight fractionation of chlorine particularly as compared with fluorine. This is a surprising result since the larger ionic radius of chlorine and its well known ability to form complex molecules should lead to greater concentration of chlorine than fluorine in residual magmas; these facts, as well as the water solubility of chlorine compounds, have been advanced as an explanation for the high

cl/F ratio obtaining in volcanic gases (Correns, 1956). The most likely explanation of this anomalous distribution is that volatiles have been lost from the magma chamber during crystallization and it is of interest, therefore, that McDougall (1964) has been led to invoke a loss of volatiles through joints in the overlying dolerites and sediments on independent grounds. The chilled contact of 5084 gives no reliable evidence on this point since it is actually depleted in chlorine relative to the bulk of both cores, and, if taken as representative of the original content of chlorine in the magma, would require the addition of chlorine during crystallization; this sample contains evidence of a subsequent alteration (McDougall, personal communication) and it is probable that chlorine was lost at this time.

Nickel:

Vogt (1923) presented extensive evidence that nickel is camouflaged by magnesium and this view has subsequently been supported by more recent authors (Wager and Mitchell, 1951; Goldschmidt, 1954). Ringwood (1955a, 1956) suggests, however, that due to similar ionic radii and electronegativities, the nickel-iron diadochy should be of paramount importance, and support for this conclusion is derived from the high abundance of nickel in iron oxides, (Wilkinson, 1959; McDougall and Lovering, 1963). On the other hand, Snyder (1959) has criticized Ringwood's discussion and favours the nickel-magnesium diadochy as the more important. In the Tasmanian dolerites at Mt. Wellington and Red Hill, the iron ore contains approximately twice as much nickel as do co-existing pyroxenes (Tiller, 1959; McDougall and Lovering, 1963) and thus the Ni-Fe⁺² diadochy might be expected to be of most importance in the Great Lake sheet.

However electron probe studies (Lovering, unpublished work) have shown that magnetite grains in some eclogitic rocks contain very small (~lp) sulphide blebs. Semiquantitative analyses using the electron probe indicate that these sulphide blebs are composed of chaleopyrite, various iron sulphides and an iron-nickel-cobalt sulphide of some type. It is not impossible that similar sulphide blebs could occur in the iron ores extracted from the Tasmanian dolerites so that the nickel (and cobalt) found in these iron ores may occur in a separate sulphide phase.

In 5123, nickel is uniformly abundant at about 115 p.p.m. at depths greater than 1000' and declines smoothly from this point to 5.5 p.p.m. Ni in the uppermost central zone dolerites; the granophyres contain nickel below the detection limit of 2 p.p.m. Ni. In 5084 nickel shows a pronounced peak in the most basic portion (200'-300') of the core and declines steadily through the central zone dolerites. The profile of nickel through both cores is very similar to that of magnesium, as has also been noted in the Mt. Wellington sill (Tiller, 1959). This is not necessarily evidence for Ni-Mg diadochy, however, since chromium also possesses a very similar profile although it is known to be replacing ferric iron.

Figure 3 shows the smooth decrease of nickel with differentiation. Nickel and chromium are the trace elements most severely affected by fractional crystallization in the Great Lake sheet, as has been found in other differentiated dolerites (Nockolds and Allen, 1956), but they differ from each other in that the decrease of chromium is more rapid than of nickel and nickel is not enriched in the final differentiates as is chromium.

If nickel is replacing magnesium, the Ni/Mg ratio should increase during differentiation whereas if it is replacing iron the Ni/Fe⁺² ratio should decrease since the ionic radius and electronegativity of nickel is intermediate between that of magnesium and iron. In fact, both ratios decrease which strongly suggests that the fractionation of nickel has proceeded independently of that of magnesium. This is in accord with the smooth curve obtained from a plot of Ni/FeO against an index of differentiation in contrast to the scatter of Ni/MgO points (Figure 4). Thus it seems probable that at least in the Tasmanian dolerites the Ni-Fe⁺² diadochy is of greater importance than that of Ni-Mg in agreement with Ringwood's (1955a) interpretation. Scandium and Cobalt:

These elements are alike in their ability to replace magnesium and di-valent iron and commonly show similar fractionation patterns during igneous differentiation (Wager and Mitchell, 1951; Nockolds and Allen, 1956). Tiller (1959) and McDougall and Lovering (1963) have shown that the iron ore contains more cobalt than do co-existing pyroxenes in the Tasmanian dolerites but since iron ore constitutes less than 5% of the total rock (McDougall, 1964) the variation of cobalt must be attributed primarily to the pyroxenes.

Both cobalt and scandium increase from the bottom of 5123 to a slight maximum in the 1200'-700' portion of the core and then slowly decrease till the appearance of granophyre when they fall abruptly. In 5084 they again parallel each other by rising slightly from the chilled contact values to form maxima in the 200'-300' portion of the core, rise to further maxima

^{*} Co may occur in separate sulphide phases included in the iron ores (see Nickel discussion).

in the uppermost lower zone dolerites and gradually decrease through the central zone. The trend of both scandium and cobalt through these cores is very similar to that of magnesium suggesting that they may be replacing Mg rather than iron in the pyroxenes. On the other hand, a similarity of profiles of the two elements does not necessarily imply that their lattice sites are identical.

The abundance of scandium and cobalt decrease with differentiation but the rate of change in the more acid differentiates appears to be somewhat greater for scandium. A similar distribution for these elements has been shown to hold for a large number of differentiated tholeitic magmas by Nockolds and Allen (1956). The Co/Mg and Sc/Mg ratios increase rapidly while the Co/Fe⁺² and Sc/Fe⁺² ratios decrease with differentiation. These ratios correspond to the result to be expected from consideration of the relevent ionic radii and electronegativities (Table 5). The ratios of cobalt and scandium with magnesium adhere somewhat more closely to a smooth curve when plotted against an index of differentiation than do their ratios with iron (Figures 5 and 6), again suggesting that they are more closely associated with magnesium than with iron.

Copper:

Copper replaces sodium and di-valent iron in silicate and oxide minerals as well as forming independent sulphide minerals (Wager and Mitchell, 1951; Snyder, 1959). In the Mt. Wellington dolerite of Tasmania, Tiller (1959) has shown that copper is present in the pyroxene, plagioclase and iron ore fractions and McDougall and Lovering (1963) have demonstrated the same distribution of copper in the Red Hill (Tasmania) granophyre; it therefore

seems probable that the Great Lake sheet also contains a distribution of copper between the silicate, oxide and sulphide minerals.

In 5123 copper is low (35-50 p.p.m.) in the lower zone dolerites, rises to a maximum of 100-150 p.p.m. in the central zone and abruptly decreases in the granophyres to 44 p.p.m. In 5084 it is depleted in the lower zone and rises to a maximum in the central zone dolerites. The distribution of copper in 5084 is very similar to that found by Tiller (1959) for the Mt. Wellington sill, whereas the distribution in 5123 parallels that found at Red Hill (McDougall and Lovering, 1963) and in the Skaergaard intrusion (Wager and Mitchell, 1951).

The rapid increase in copper content with differentiation to a maximum at a mafic index of 70-80 followed by an abrupt decline is shown clearly in Figure 2. The peak in copper abundance preceding the appearance of granophyre has been attributed to the separation of an impliscible sulphide phase (Wager and Mitchell, 1951; McDougall and Lovering, 1963) and appears to be a general accompaniment to magmatic fractional crystallization.

Gallium:

Gallium is commonly camouflaged by tri-valent iron and aluminium during magmatic differentiation and occurs predominantly in the feldspars and magnetite (Shaw, 1957). In the Great Lake sheet, magnetite is present at 5% while plagioclase constitutes 40-50% of the rock (McDougall, 1964) and thus the feldspar would be expected to account for virtually all of the gallium.

Gallium decreases with depth through nearly the entire length of 5123; it falls rapidly from 33 p.p.m. Ga at 10' to 19 p.p.m. Ga at 200' and decreases more slowly to 6.2 p.p.m. Ga at 1400', after which it begins to rise

again. In 5084, the gallium content decreases from the chilled contact value of 13 p.p.m. Ga to a minimum of 8.5 p.p.m. Ga at a height of 195' after which it increases to a maximum of 20 p.p.m. Ga in the upper part of the core. It is apparent that gallium was greatly concentrated in the residual magma during crystallization differentiation and, in fact, the degree of gallium fractionation in 5123 very closely approximates that of the Skaergaard intrusion; in the latter, Wager and Mitchell (1951) record a range of 8 to 35 p.p.m. Ga in rocks originating from a parent magma containing 17 p.p.m. Ga.

When the data from both drill cores are combined and plotted against an index of differentiation, it may be seen that gallium increases linearly with differentiation (Figure 1). The Ga/Al (Table 4) ratio also increases with differentiation as is common in tholeittic magmas (Wager and Mitchell, 1951; Nockolds and Allen, 1956) and probably reflects the greater radius and electronegativity of gallium with respect to aluminium.

Chromium:

Chromium is camouflaged by ferric iron in magnetite and pyroxenes and may form an independent chrome-spinel mineral at concentrations as low as 250 p.p.m. Cr in the magma (Wager and Mitchell, 1951). McDougall and Lovering (1963) have shown that in the Red Hill dolerite, the iron ore contains more chromium than does co-existing pyroxene but the total rock contains almost twice as much chromium as can be accounted for by the pyroxenes and iron ore; they were unable to decide whether this reflected an analytical bias or the presence of chromite. Nevertheless, the preponderance of pyroxene in the Great Lake sheet (McDougall, 1964) indicates that the variation of chromium in the rock is predominantly due to the pyroxenes.

The chromium content of 5123 falls rapidly from the high abundance in the deepest portion of the core to a plateau of approximately 10 p.p.m. Cr in the central zone dolerites and is absent (<2 p.p.m.) from the final granophyre at a depth of 10'. In 5084, chromium is greatly enriched in the most basic part of the core (100'-300') and declines steadily through the central zone dolerites. The extreme fractionation of chromium invariably attends magmatic differentiation (Nockolds and Mitchell, 1946; Wager and Mitchell, 1951; Nockolds and Allen, 1956) and is usually attributed to the smaller size and electronegativity of the Cr⁺³ ion relative to Fe⁻³ leading to enrichment of the early crystals in chromium and consequent rapid depletion of the magma.

The rapid decrease of chromium with differentiation is clearly shown in Figure 3 which also indicates a slight increase of chromium in the final differentiates. The final enrichment of chromium has been attributed to a change in oxidation state (Wager and Mitchell, 1951) and to the formation of a complex (Ringwood, 1955b). The change in properties of chromium is also shown by the Cr/Fe⁺³ ratio (Table 4) which decreases sharply at first but remains essentially constant in the later differentiates.

Vanadium:

Vanadium is usually concentrated in the iron ore fraction of silicate rocks in which it replaces titanium and iron and, to a lesser extent, in the pyroxenes replacing tri-valent iron. Tiller (1959) has shown that in the Mt. Wellington sill (Tasmania) the ore contains 3-4 times as much vanadium as do co-existing pyroxenes and a similar distribution can be expected for the Great Lake sheet.

Vanadium is remarkably constant in the dolerites of 5123, showing only a slight maximum in the 800'-900' portion, and decreases abruptly in the granophyres. It is more variable in 5084 in that it is slightly enriched in the most basic 200'-300' portion of the core and declines in the central zone dolerites. Tiller (1959) has described a similar distribution in the Mt. Wellington dolerites. The uniform abundance of vanadium in the Tasmanian dolerites is in marked contrast to the strong fractionation exhibited in the Skaergaard (Wager and Mitchell, 1951), Dillsburg (10tz, 1953), and most other differentiated tholeittis (Nockolds and Allen, 1956), and probably reflects the very minor and rather constant amount of ore obtaining in the Great Lake dolerites.

In accord with this distribution, vanadium changes little with differentiation until the abrupt decrease in the granophyre (Figure 2). The great impoverishment of the granophyre in vanadium is due to the steady depletion of the magma since most of the 5123 core contains slightly more vanadium than the original magma as represented by the chilled margin of 5084. The ionic radius and electronegativity of quadri-valent vanadium is less than that of ferric iron and thus the V/Fe^{+3} ratio is expected to decrease during differentiation and this is found to be true of these rocks. The V/Ti ratio is also expected to decrease during differentiation due to the smaller radius of V^{+4} and the observation that this ratio adheres more closely to a smooth curve with differentiation than does the V/Fe^{+3} ratio (Figure 7) suggests that vanadium is more closely associated with titanium than with ferric iron in the Great Lake sheet.

Barium:

The ionic radius of barium is such that it may be camouflaged by calcium or captured by potassium bearing minerals and its fractionation

during differentiation is generally very similar to that of potassium

(Wager and Mitchell, 1951; Nockolds and Allen, 1956; Notz, 1953).

The barium content of 5123 decreases rapidly with depth from 550 p.p.m. at 50° to 120 p.p.m. at 1200° after which it remains essentially constant. In 5084, it falls abruptly from the chilled contact value of 500 p.p.m. to 200 p.p.m. and begins a gradual rise at the 250° height. If the chilled contact of 5084 is taken as representative of the composition of the original magma, it is apparent that barium must have been lost during crystallization since only the granophyres of 5123 contain as much barium as the original abundance. McDougall (personal communication) considers the 5084 contact to be slightly altered, however, and it may be that barium has been added to this sample during the alteration.

The great enrichment of the residual magma in barium is clearly shown in Figure 1 where the combined data are plotted against an index of differentiation. The fractionation of barium is similar to that of potassium in these cores but this does not necessarily indicate their occupation of identical lattice sites. The Ba/K ratio is highly variable and shows no discernible trend with differentiation whereas the Ba/Ca ratio defines a smooth curve increasing with differentiation (Figure 8). This strongly suggests that the barium is present in the plagioclase and therefore varies independently of potassium. The increase of the Ba/Ca ratio may be attributed to the greater radius of barium which causes its preferential exclusion from the early crystallates.

Strontium:

The strontium-calcium diadochy is well known and results in the concentration of strontium in the plagioclase fraction of a rock (Nockolds and Mitchell, 1945; Wager and Mitchell, 1951).

The strontium content of the Great Lake sheet has been only slightly affected by differentiation. Strontium falls from 190 p.p.m. in the granophyre of 5123 to a minimum of 98 p.p.m. in the lower zone dolerites; in 5084 it falls from the chilled contact value of 150 p.p.m. to 100 p.p.m. Sr in the most basic rock before rising slowly to a maximum of 170 p.p.m. in the central zone dolerites. In the Skaergaard intrusion, strontium rises to a maximum before decreasing in the granophyre fraction (Wager and Mitchell, 1951) and the same pattern has been found for the differentiated dolerite of Dillsburg (Notz, 1953), but if such a maximum is present in the Great Lake sheet it is too small to detect.

The increase of strontium with differentiation is shown in Figure 1 to be curvilinear with the greatest rate of change at low mafic index values; again there is no indication of a maximum preceding the granophyre stage. The Sr/Ca ratio (Table 4) also increases with differentiation and the increase is most rapid in the final differentiates. This may be attributed to the larger size of the strontium ion and is invariably found in differentiated sequences (Nockolds and Mitchell, 1946; Wager and Mitchell, 1951; Nockolds and Allen, 1956).

DISCUSSION

Comparison of the Great Lake Magma with Other Tholeittic Basalts. The chilled margin of an intrusion is generally accepted as an approximation to the composition of the original magma. Table 6 compares trace element concentrations of the lower contact of 5084 with similar samples from other tholeittic basalts and with the "average basalt" of Turekian and Wedepohl (1961).

Unfortunately, McDougall (personal communication) has found evidence of a slight hydro-thermal alteration in this sample and thus the value of such a comparison may be somewhat dubious; in fact, comparison of these results with the distribution found in the two cores strongly suggests that barium has been added and chlorine lost from this sample. Nevertheless, Table 6 indicates the general similarity of the assumed Great Lake magma to other Tasmanian magmas (in so far as comparison is possible) that might be expected. It contains considerably less Ni, Co, Cr and Cu than do the Hawaiian, Karroo and Skaergaard dolerites and rather more Sc. Except for the depletion of strontium, the Great Lake sheet compares remarkably closely with the average basalt.

Lattice Sites Occupied by Fluorine and Chlorine. Since the behaviour of the halogens during differentiation has not previously been studied, it is of some interest to determine their mode of occurrence in the Great Lake sheet. Fluorine and chlorine normally occur in apatite at hydroxyl lattice sites; fluorine can also form fluorite or replace oxygen while chlorine can occur independently in sodalite and scapolite. It has been noted previously that there is insufficient phosphorus in the Great Lake sheet to account for either of the halogens as apatite and thus if it can be shown that fluorine and chlorine are occupying identical lattice sites they must be replacing the hydroxyl ion. Examination of thin sections has failed to detect any of the independent fluorine and chlorine minerals (McDougall, personal communication) but this is not conclusive and a multi-variate statistical technique will be employed to show that chlorine and fluorine do in fact occur in the same lattice site.

It has been stressed previously that similar concentration trends of two elements with depth or index of differentiation does not necessarily imply an identity of lattice sites. It is therefore necessary to consider the residual variations after removal of the effects produced by differentiation. To do this, we assume that the observed abundance $Z_{i'}$, $(Z_1 = \log C_1, Z_2 = \log F)$ at any depth D in the core is the sum of three independent functions: the depth of the sample; the availability of lattice sites, $S_{i'}$; and the analytical error of the determination, $S_{i'}$. Therefore $Z_{i'}$ if $(D_{i'}) + h(S_{i'}) + g(S_{i'})$. It is obvious that $f(D_{i'})$ and $h(S_{i'})$ are not actually independent functions but $h(S_{i'})$ may be considered as random variations of lattice sites whereas $f(D_{i'})$ may be attributed to the smooth variation with differentiation. Thus we further assume that $f(D_{i'})$ is a simple, smooth curve and that the observed scatter of the data represents irregularities of crystallization from the magma and analytical error. The removal of the effect of $f(D_{i'})$ on $Z_{i'}$ then yields two new functions: $Z_{i'}^{i'} = g(S_{i'}) + h(S_{i'})$.

Fluorine and chlorine were determined independently of each other and thus the analytical errors of the determinations cannot be correlated, implying that $g(X_1)$ and $g(X_2)$ are completely independent functions. Therefore, any relationship found between Z_1 ' and Z_2 ' must reflect a relationship between $h(S_1)$ and $h(S_2)$ implying that the small scale variations of fluorine and chlorine lattice sites are identical, which in turn suggests that the sites are in fact identical.

The first problem then, is the computation of $f(D_{\underline{j}})$. Observation of the profiles of fluorine and chlorine with depth in 5123 (Figure 9) suggests that the general trend of the data may be satisfactorily approximated with a parabola. With this assumption, $f(D_{\underline{j}})$ may be computed by standard least square methods (Ezekial and Fox, 1959). It should be noted that the abundance values

have been transformed to their logarithms in order to satisfy the statistical requirement of homocedacity since it is known from experimental considerations that the analytical error of both determinations is distributed approximately log-normally. The curves finally arrived at are:

$$\log F = 2.814 - 6.3208 \times 10^{-4}D + 2.3875 \times 10^{-7}D^2$$

 $\log C1 = 2.0605 - 5.4648 \times 10^{-4}D + 3.0254 \times 10^{-7}D^2$

These are shown plotted with the observed Z_{1} in Figure 9. From these parabolas a "calculated" abundance of the halogens may be obtained at any depth which, when subtracted from the "observed" abundance, yields the Z_{1} values.

Given these values of $Z_{\underline{A}}^{-1}$, a least squares straight line of the form $Z_{\underline{A}}^{-1} = A + BZ_{\underline{A}}^{1}$ may be fitted to these data. This has been done by standard techniques to yield:

$$(\log F)' = 0.0039 + 1.0015 (\log C1)'$$

The correlation coefficient computed from these data indicates a highly significant relationship between the Z'z functions and thus, in view of the preceding discussion, the inference that fluorine and chlorine are occupying identical lattice sites appears to be warranted. The coefficients of this equation are of some interest. The computed value of A does not differ significantly from zero which indicates that when no chlorine sites are available, there are no fluorine sites; the coefficient B does not differ significantly from one indicating that an increase of chlorine sites yields an equal increase of fluorine sites. Thus both coefficients agree in the implication of an identity of fluorine and chlorine lattice sites. Although no hydroxyl minerals have been observed in thin section, it appears probable therefore that they do exist as sub-microscopic inclusions in the mesostassis and that

they do contain most of the fluorine and chlorine present in the Great Lake dolerite.

Small Scale Variation in the Cores. McDougall (1964) has noted the presence of a finer scale variation in the Great Lake dolerites and specifically cites the abnormally low MgO content of the 900' sample of 5123. To further determine the extent of this "ripple", samples from 890' and 950' were also included in the trace element study. The 900' sample contains less Cr, Sc, V, Ni and Co and more Ga, Sr, F and Cl than either the 890' or 950' samples confirming the irregular variation in this region of the core. From the profiles there appears to be a rather gradual increase of "acidity" from 1000'-900', an abrupt decrease between 900'-890', followed by the gradual increase through the central zone dolerites. Thus, the variation is limited to 100' and may be considerably less. Small scale variations such as this are probably of frequent occurrence in these dolerites and a more detailed study of them than was possible here might be of considerable interest.

CONCLUSION

The general fractionation of trace elements in the Great Lake dolerites is similar to those found in most differentiated basic tholeitic magmas. Nickel and chromium become greatly depleted and cobalt and scandium slightly depleted in the residual magmas. Vanadium decreases only slightly with differentiation but is virtually exhausted by the granophyre stage. Copper rises rapidly with differentiation to a maximum and is then removed, presumably by separation of an immiscible sulphide phase. Strontium increases slightly and fluorine, barium and gallium increases greatly with differentiation. Chlorine may increase slightly in these dolerites but it appears probable that chlorine has been lost with other volatiles during crystallization

of the Great Lake sheet.

In these dolerites, it is believed that Ni occupies Fe⁺² sites,

Co and Sc replace both Mg and Fe⁺²; Cr replaces Fe⁺³ until the later stages
when a change of oxidation state probably occurs; V⁺⁴ replaces Ti⁺⁴; Ba and

Sr replace Ca in the plagioclase; Ca replaces Al, while F and Cl occupy
hydroxyl sites in the poorly crystallized material of the mesostassis.

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TABLE 1.
SPECTROGRAPHIC PRECISION

Element	Mean (p.p.m.)	Relative Error
Ba	329	5.7
Sr	157	3.6
Sc	40.8	14.9
V	196	5.2
Cu	127	9.8
Cr	15.1	9.8
Ga	19.1	10.9
Ni	29.6	7.0
Co	42.0	6.5

Statistics calculated from 14 single arcings of a dolerite (D.D.H. 5084, 1035) distributed throughout the sample exposures.

TABLE 2

ANALYTICAL RESULTS FOR THE 5123 CORE

Dolerite Type	Granophyre			Central		Zone		Dolerites					Lower		Zone		Dolerites					
Mafic Index*	ŧ	91.4	84.1	83.2	81.2	74.3	69.2	63.5	60.5	55.1	ı	59.3	1	47.5	44.5	43.0	41.2	41.0	41.4	45.6	43.0	
Sr	190	170	200	160	160	140	160	140	140	130	130	140	120	120	120	100	100	66	100	86	120	
Ba	200	550	510	380	400	280	340	260	220	220	200	700	150	160	170	130	150	130	130	130	160	
mdd A	9.7	37	220	190	190	190	210	210	210	270	250	210	230	250	240	230	230	210	220	220	220	
Cr ppm	2	12	9.6	11	8.2	9.6	15	17	35	99	9	38	80	120	190	220	340	200	490	240	370	
Sc	20	22	38	28	94	7 7	40	48	7 46	29	26	87	64	26	28	55	52	64	20	20	67	
Ga ppm	33	31	27	19	18	18.5	18	11.5	14.5	16	11.5	13	8.6	9.4	8.4	8.7	6.8	6.2	10.5	6.9	. 3	
Cu	77	77	155	130	130	155	170	120	79	. 93	98	9	19	67	48	45	36	37	77	42	87	
Co	22	27	34	32	35	41	36	43	77	. 56	54	39	59	51	52	20	97	45	7.7	74	29	
Ní ppm	7	7	5.5	0.9	9.5	18	34	46	52	82	91	51	88	105	115	120	125	110	135	120	120	
C1 ppm	120	105	65	83	101	81	91	72	78	55	20	82	75	71	69	79	9	85	75	7.7	111	
F Ppm	630	610	610	480	510	340	360	330	300	260	210	360	270	250	315	255	240	240	310	230	260	
Depth (Ft.) from Surf-	10	20	100	200	300	400	500	009	700	800	890	006	950	1000	1100	1200	1295	1400	1500	1600	1735	

* Data from McDougall, 1964

TABLE 3

ANALYTICAL RESULTS FOR THE 5084 CORE.

Dolerite Type	Chilled	Margin		Lower		Zone		Dolerites				Central	Zone	Dolerites
Mafic Index*	56.9	54.6	50.8	44.1	6.84	9.97	44.4	0.94	57.4	53.1	56.8	9.59	7.99	73.0
Sr ppm	150	120	120	100	120	120	120	120	130	130	140	170	160	150
Ba	200	200	200	140	190	190	160	190	200	220	250	310	330	300
V Dpm	200	180	200	190	200	240	200	230	190	220	240	200	200	190
Cr ppm	120	120	150	330	190	390	230	240	87	120	100	18	15	80
Sc ppm	40	77	97	45	97	27	20	54	41	51	52	40	41	53
Ga	13	11	12	9.4	10.5	8.6	13.5	8.6	14.5	10.2	13	20	19	13
Cu	7.5	75	99	47	55	55	87	84	78	75	86	130	130	115
CO Co	42	43	77	77	43	55	20	77	39	97	47	37	42	39
Ni ppm	. 29	83	78	135	95	130	125	105	61	84	9/	39	30	21
CI ppm	72	99	84	78	55	09	98	73	71	74	87	80	63	72
균 m m	390	270	360	300	310	270	310	320	240	325	250	390	360	350
Height (Ft.) Above Lower Contact	П	67	95	132	151	195	248	300	370	435	635	834	1035	1180

* Data from McDougall, 1964

TABLE 4

TRACE ELEMENT - MAJOR ELEMENT RATIOS.

			· · · · · · · · · · · · · · · · · · ·		· · · · · · · · · · · · · · · · · · ·	
afic ndex	$\frac{\text{Ni} \times 10^4}{\text{FeO}}$	$\frac{\text{Ni} \times 10^4}{\text{MgO}}$	Co x 10 ⁴ FeO	Co x 10 ⁴ MgO	Sc x 10 ⁴ Fe0	Sc x 10 ⁴ Mg0
.0	15.3	10.1	6.27	4.1	5.83	4.5
1.2	18.1	11.7	6.68	4.3	7.56	4.9
.4	17.6	11.8	6.13	4.1	6.52	4.4
. 6	15.9	10.8	6.23	4.2	6.64	4.5
0	15.9	11.1	6.62	4.6	7.28	5.1
0	16.4	11.9	8.106	5.8	6.69	4.8
1	18.5	12.9	6.04	4.2	6.18	4.3
4	17.7	12.8	7.08	5.1	7.08	5.1
. 5	14.8	11.2	6.72	5.1	7.48	5.7
.0	14.1	10.9	5.92	4.6	7.28	5.6
6	18.0	13.5	7.63	5 .7	7.90	5.9
5	13.4	10.8	6.52	5.2	7.16	5.7
9	12.8	10.4	5.80	4.7	6.21	5.0
8	9.8	9.5	5.54	5.4	5.80	5.6
1	10.9	10.7	5.96	5.9	6.61	6.5
6	10.3	11.5	5.34	5.9	5.46	6.1
1	9.0	9.7	6.14	6.6	6.47	7.0
8	9.3	10.8	5.78	6.7	6.38	7.4
9	9.0	9.7	5.66	6.1	5.39	5.8
4	8.6	10.1	5.52	6.5	5.81	6.8
. 3	7.0	. 9.7	5.33	7.5	6.56	9.2
. 5	6.1	8.5	4.92	6.9	5.38	7.5
5	5.7	8.8	5.00	7.8	5.57	8.7
. 6	4.8	8.1	4.55	7.7	4.92	8.3
. 4	3.8	6.7	5.28	9.4	5.15	9.2
2	4.1	8.4	4.32	8.9	4.80	9.9
0	2.6	5.6	4.87	10.4	6.62	14.1
3	2.2	5.2	4.88	11.7	5.24	12.6
. 2	1.2	4.0	4.43	14.8	5.82	19.5
. 2	0.72	3.1	3.86	16.6	3.38	14.5
. 1	0.63	2.6	3.91	16.0	4.37	17.9
4	-	-	2.96	19.3	2.41	19.3

TABLE 4 (Cont'd)

Mafic Index	$\frac{\text{Cr x } 10^3}{\text{Fe}_2^{\ 0}_3}$	$\frac{v \times 10^2}{\text{Fe}_2 \text{O}_3}$		$\frac{\text{Ga} \times 10^4}{\text{Al}_2\text{O}_3}$	$\frac{\text{Ba} \times 10^2}{\text{K}_2\text{O}}$	Ba x 10 ³	$\frac{\text{Sr x } 10^3}{\text{CaO}}$
41.0	50.0	5.26	4.56	0.46	1.91	1.04	0.79
41.2	59.6	4.04	4.79	0.49	1.78	1.22	0.81
41.4	110	5.00	4.40	0.83	2.13	1.08	0.83
42.6	33.8	3.10	4.59	0.50	2.07	1.08	0.81
43.0	36.7	3.84	4.79	0.66	2.10	1.06	0.82
43.0	119	7.10	4.23	0.56	2.08	1.33	1.00
44.1	34.4	1.98	4.04	0.69	1.32	1.21	0.86
44.4	30.7	2.67	4.00	0.92	2.50	1.39	1.04
44.5	39.6	5.00	4.62	0.62	2.30	1.42	1.00
46.0	30.8	2.95	4.60	0.72	2.93	1.64	1.04
46.6	31.4	1.93	5.00	0.60	2.47	1.65	1.04
47 . 5	12.0	2.50	5.20	0.73	1.95	1.39	0.96
48.9	14.3	1.50	3.84	0.75	2.37	1.69	1.07
50.8	26.8	3.57	3.64	0.73	2.95	1.81	1.07
53.1	10.6	1.95	3.67	0.70	1.96	2.00	1.18
54.6	19.0	2.86	2.73	0.75	1.94	1.83	1.10
55.1	4.4	2.12	4.65	1.25	2.75	1.94	1.15
56.8	9.4	2.26	3.43	0.85	2.61	2.23	1.25
56.9	7.3	1.22	2.60	0.88	-	-	1.46
57.4	8.1	1.76	3.17	0.85	2.44	1.69	1.10
59.3	12.3	6.78	3.75	0.72	1.46	1.63	1.14
60.5	4.2	2.53	2.91	0.93	1.92	2.00	1.27
63.5	1.7	2.10	2.84	0.75	2.13	2.43	1.31
65.6	1.9	2.06	2.98	1.22	2.70	2.98	1.64
66.4	1.7	2.30	3.18	1.16	2.57	3.25	1.58
69.2	1.9	2.66	2.19	1.08	2.52	3.40	1.60
73.0	0.4	.88	2.40	0.84	2.68	2.91	1.45
74.3	0.56	1.11	2.26	1.13	2.03	2.98	1.49
81.2	0.35	.81	1.76	1.14	2.63	4.50	1.80
83.2	0.65	1.12	1.79	1.16	2.50	4.47	1.88
84.1	0.38	.87	1.76	1.77	2.66	6.74	2.64
91.4	0.40	.12	0.31	2.71	2.33	10.5	3.23

TABLE 5.

RADIUS AND ELECTRONEGATIVITY

OF A NUMBER OF IONS.

Ion	Radius, A	Electronegativity
Fe ^{† 2}	•74	1.65
Mg ⁺²	.66	1.2
Ni ⁺²	•69	1.7
Co ⁺²	•72	1.7
Sc ⁺³	.81	1.3
Fe ⁻³	•64	1.8
Cr ^{→3}	•63	1.6
V+3	•74	1.35
V+4	•63	1.6
ri ⁻⁴	•68	1.6
Ga ^{∓3}	.62	1.6
A1 ⁺³	•51	1.3
Ca ⁺²	•99	1.0
Ba ⁺²	1.34	•85
Sr ^{÷2}	1.12	1.0
ĸ	1.33	.8
P-	1.36	-
cı-	1.81	•
0-2	1.40	

Data from Ringwood (1955a) and Green (1959).

COMPARISON OF GREAT LAKE MAGMA
WITH OTHER THOLEIITIC

TABLE 6.

BASALT MAGMAS.

3					Parts	per 1	millior	1.				
Sam- ple	F	Cl	Ва	Sr	Ni	Co	Cr	Se	V	Cu	Ga	
A	390	72	>500	150	67	42	120	40	200	75	13	
В	270	-	-	-	93	47	151	-	-	78	-	
С	-	_	-	_	88	51	-	-	380	105	22	
D	-	-	60	3 5 0	3 5 0	55	500	10	300	-	25	
E	_	-	70	125	150	50	425	20	220	-	30	
F	-	•	170	200	60	55	250	40	275	***	20	
G	-	-	80	178	18	42	63	57	475	-	25	
Н	_	-	350	350	30	30	45	20	300		25	
I	-	_	125	400	87	35	200	-	250	170	-	
J	-	-	43	350	170	53	170	12	140	130	17	
K	400	60	330	465	130	48	170	30	250	87	17	

A: Great Lake Sheet, Chilled Contact of 5084.

B: Red Hill, McDougall and Lovering, 1963 (F determined here).

C: Mt. Wellington, Tiller, 1959.

D: Hawaiian Tholeiitic Basalts

[·] E: Karroo Dolerites

F: British Tertiary Tholeitic) Nockolds and Allen, 1956.

G: Nakone Volcanics

H: Northfield Sill

I: Dillsberg Dolerite, Notz, 1953.

J: Skaergaard, Wager and Mitchell, 1951.

K: Average Basalt, Turekian and Wedepohl, 1961.

FIGURE CAPTIONS

- Figure 1. Variation of F, Cl, Ga, Ba, and Sr with differentiation in the Great Lake sheet.
- Figure 2. Variation of Cu, V, Co, and Sc with differentiation in the Great Lake sheet.
- Figure 3. Variation of Ni and Cr with differentiation in the Great Lake sheet.
- Figure 4. Variation of the Ni/FeO and Ni/MgO ratios with differentiation in the Great Lake sheet.
- Figure 5. Variation of the Co/FeO and Se/MgO ratios with differentiation in the Great Lake sheet.
- Figure 6. Variation of the Sc/FeO and Sc/MgO ratios with differentiation in the Great Lake sheet.
- Figure 7. Variation of the V/Fe₂0₃ and V/TiO₂ ratios with differentiation in the Great Lake sheet.
- Figure 8. Variation of the Ba/K₂0 and Ba/CaO ratios with differentiation in the Great Lake sheet.
- Figure 9. Variation of F and Cl with depth in the D.D.H. 5123 core showing the least-squares fitted parabolas.















